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IMPROVED NON-METALLIC MATERIALS FOR  
ELECTRONIC APPLICATION

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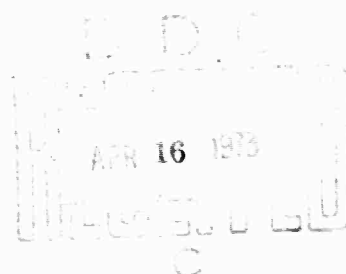
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TECHNICAL SUMMARY REPORT  
TO  
ADVANCED RESEARCH PROJECTS AGENCY  
ON

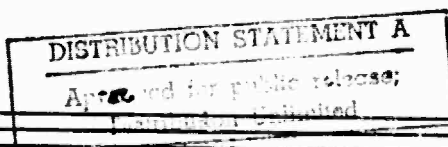


IMPROVED NON-METALLIC MATERIALS FOR ELECTRONIC APPLICATION

For the Period 1 July 1972 to 31 December 1972

Contract No. DA-49-083 OSA 3140, Amendment No. P00006

ARPA Order No. 338/7



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THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY  
UNIVERSITY PARK, PENNSYLVANIA

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Improved Non-Metallic Materials for Electronic Application

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## Part 1: INTRODUCTION

### 1.1 FORMAT

This semi-annual report covers briefly the work supported under the ARPA contract dealing with "Improved Non-Metallic Materials for Electronic Application." The Annual Report of the Laboratory issued at the end of the fiscal year reports the results obtained in this ARPA supported work as well as all other research on materials carried out by the faculty of the Materials Research Laboratory. The scope of this report is therefore considerably narrower than that of the Annual Report, while at the same time it generally contains more detail than the latter.

Continuing the major departure from previous years, the research reported here represents a much more task-oriented study in two defined areas. The principal rationale underlying both major areas is the theme that the chemical side of materials science has reached a maturity where it is increasingly within the reach of the laboratory to tailor materials with designed properties.

The first area deals with electrooptic materials. We can now grow single crystals of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  in the correct platy habit and are working to optimize the growth condition. The new ferroelastic materials isopropyl ammonium chloroplatinate and isopropyl ammonium chlorostannate have been grown as quite good quality crystals and many properties have been measured.

The main effort of the past year has gone into preparation of coatings on crystals and glasses and their characterization. RF sputtering has been shown to be a tremendously versatile tool for the preparation of both crystalline and noncrystalline layers of many compositions. By controlling process parameters in the sputtering chamber, composition and valence state in the sputtered layers can be controlled. Glass surface coatings and glass surface strengthening have been prepared by CVD, microwave plasma, and ion exchange techniques. Raman spectroscopy has emerged as an interesting new tool for structural analysis of bulk glass and the near-surface layers. The technique demonstrates that there is a range of average order in different glasses with an average periodicity. Phase separation and the onset of crystallization are also manifested in the spectra.

## 1.2 COMMUNICATION

The ARPA-supported work of previous years continues to be reflected in the production of theses and research papers. Six graduate students completed Ph.D's during 1972 with all or partial support from ARPA. Their thesis titles are listed below. Papers reporting the results of the past year's work are already beginning to appear along with final write-ups of work done under earlier sponsorship several years ago.

### 1.2.1 Theses

Joseph F. Balascio

"The Growth and Characterization of Single Crystal Calcite,"  
Ph.D. in Solid State Science, 1972.

Edward C. Beahm

"Laser Mass Spectrometric Study of Inorganic Materials,"  
Ph.D. in Chemistry, 1973.

Vassilis G. Keramidas

"Raman Scattering and the Characterization of Order-Disorder  
in Polycrystalline Solids," Ph.D. in Solid State Science, 1973.

Russell F. Messier

"New Experimental Approach to Understanding Formation of Non-  
Crystalline Solids," Ph.D. in Solid State Science, 1973.

Michael P. O'Horo

"Insulator to Semiconductor Conversion in  $\text{CdF}_2$ ," Ph.D. in  
Solid State Science, 1972.

Takeshi Takamori

"Rapid Crystallization Behavior of Non-Crystalline Solids,"  
Ph.D. in Solid State Science, 1972.

### 1.2.2 Publications in 1972

J.F. Balascio and W.B. White, "Hydrothermal Growth of Calcite From  
Alkali Carbonate Solutions," Mat. Res. Bull. 7, 1461-1472  
(1972).

V.G. Keramidas and W.B. White, "Raman Spectra of Oxide with the  
Fluorite Structure," J. Chem. Phys. (in press).

V.G. Keramidas and W.B. White, "Raman Scattering From  $\text{Ca Zr}_{1-x}\text{O}_{2-x}\square_x$ ,  
a System with Massive Point Defects," J. Phys. Chem. Solids  
(submitted).

V.G. Keramidas and W.B. White, "Raman Scattering Study of the  
Crystallization and Phase Transformation of  $\text{ZrO}_2$ ," J. Amer.  
Ceram. Soc. (submitted).

- B.E. Knox, "Laser Ion Source Analysis of Solids," Chap. 4 in Trace Analysis by Mass Spectrometry, A.J. Ahearn, editor, Academic Press, N.Y. 1972.
- R. Messier, T. Takamori and R. Roy, "Structural Differences among Different Non-Crystalline Ge-Te Phases," J. Non-Cryst. Solids 8-10, 816-822 (1972).
- R. Messier and R. Roy, "Characterization of Sputtered Films in the System Ge-Te," to be submitted, J. Amer. Ceram. Soc.
- R. Messier, T. Takamori and R. Roy, "Preparation and Characterization of Non-Crystalline Ge which Crystallizes 'Explosively' at Room Temperature," to be submitted, J. Non-Cryst. Solids.
- M.P. O'Horo, A.L. Frisillo and W.B. White, "Lattice Vibrations in  $\text{MgAl}_2\text{O}_4$  Spinel," J. Phys. Chem. Solids 34, 23-28 (1972).
- M.P. O'Horo and W.B. White, "Resonance Raman Spectra of Semi-Conducting  $\text{CdF}_2:\text{In}^{3+}$  Crystals," Phys. Rev. (in press).
- R. Roy and W.B. White, "Growth of Titanium Oxide Crystals of Controlled Stoichiometry and Order," J. Cryst. Growth 13-14, 78-83 (1972).
- T. Takamori, R. Messier and R. Roy, "New Non-Crystalline Ge which Crystallizes 'Explosively' at Room Temperature," Appl. Phys. Lett. 20 (5), 201-203 (1972).
- T. Takamori and R. Roy, "Preparation of Thin Glass Films for Transmission Electron Microscopy by Splat-Cooling," J. Amer. Ceram. Soc. 55 (10), 538-539 (1972).
- T. Takamori and R. Roy, "Effect of Oxygen on Structure Properties of Quenched Ge-Te Melts," J. Mat. Sci. (in press).
- T. Takamori, R. Messier and R. Roy, "Triboluminescence on Crystallization of Non-Crystalline Ge Films," submitted to J. Mat. Sci.
- T. Takamori, R. Messier and R. Roy, "Phenomenology of the 'Explosive' Crystallization of Non-Crystalline Germanium Thick Films,"
- T. Takamori and R. Roy, "Rapid Crystallization Behavior of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  Glasses," submitted to J. Amer. Ceram. Soc.

## Part 2. FERROELECTRIC AND FERROELASTIC MATERIALS FOR

### INFORMATION AND ENERGY STORAGE AND DETECTION

#### 2.1 BISMUTH TITANATE MATERIALS

##### 2.1.1 Phase Equilibria in $\text{Bi}_2\text{O}_3\text{-TiO}_2$ System

(R.L. Mohler and W.B. White)

Several discrepancies are present in the literature concerning the number of compounds that exist in the  $\text{Bi}_2\text{O}_3\text{-TiO}_2$  binary system. Information about melting behavior and temperature, and liquidus curve data are also uncertain or lacking. Because of this, the phase equilibria in the  $\text{Bi}_2\text{O}_3\text{-TiO}_2$  system were investigated with particular emphasis being placed on the region of the diagram used in the growth of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  crystals from bismuth oxide-rich fluxes.

Various compositions were prepared and the samples annealed at constant temperatures below those needed to produce a liquid phase. The samples were then quenched from the annealing temperatures and examined by optical microscopy and x-ray diffraction. A revised liquidus curve was determined by DTA techniques. This system has proved very difficult to work with because of the volatility of the  $\text{Bi}_2\text{O}_3$  component and because of the difficulty in distinguishing the bismuth titanate phases.

##### 2.1.2 Crystal Growth of Bismuth Titanate

(D. Tiche and K.E. Spear)

Two types of crystal growth experiments have been performed on bismuth titanate. Both involved the growth of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  crystals out of a bismuth oxide rich flux. In the first type of experiment, bismuth titanate crystals were induced to grow on a thorium oxide rod that was lowered into a melt contained in a thorium oxide crucible. In the second type of experiment a solution contained in a platinum crucible with a lid was slowly cooled until an appreciable number of bismuth titanate crystals had grown. The crystals were then separated from the solution by pouring out the excess molten flux. These experiments are described in more detail below.



Compatibility studies performed last year showed  $\text{ThO}_2$  to be a suitable crucible material for containing liquid bismuth oxide and solutions of  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$ . A thorium oxide crucible containing a mixture of titanium and bismuth oxides was first heated to  $1200^\circ\text{C}$  to insure the formation of a homogeneous liquid solution, and was then slowly cooled until crystals started to form on the surface of the melt. The thermal gradient across the crucible was adjusted so that the bottom was hotter than the top, which caused the first crystals to grow on the melt surface. After the first crystals were observed, a small  $\text{ThO}_2$  rod was lowered into the melt by means of Czochralski crystal pulling equipment. Small crystals grew on this rod as well as on the crucible walls. The crystals on the rod were separated from the flux by pulling the rod out of the melt. The properties of these crystals are currently being examined to determine if they are different from those of crystals grown in platinum crucibles. One of the problems with the use of  $\text{ThO}_2$  crucibles relates to the fact that they are easily cracked by thermal shock. Extreme care must be taken in heating and cooling these crucibles.

The second type of experiment for growing  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  crystals involved the same flux system as used above and a crucible of platinum instead of  $\text{ThO}_2$ . A mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  was heated in a covered crucible to about  $1200^\circ\text{C}$  and left at this temperature for times ranging from two hours to two days. The thermal gradient across the crucible was adjusted so that the bottom was cooler than the top. After soaking the melt at  $1200^\circ\text{C}$ , the temperature of the furnace was lowered at rates ranging from 5 to  $30^\circ$  per hour by means of a temperature programmer. When the bottom of the crucible was at  $890$  to  $950^\circ\text{C}$ , the furnace was quickly raised off the crucible by a counter-weighted pulley system, the excess molten flux was poured off, and then the crucible was placed back on its pedestal and the furnace lowered into place. This process required 10 to 15 seconds. The crucible and crystals were then slowly cooled to about  $400^\circ\text{C}$ , and then the furnace was raised off the crucible for the final cooling to room temperature.

The above experiments yielded single crystal platelets of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  up to  $2 \text{ cm}^{-2}$  in size. Several observations about the growth of these crystals were made. First, neither the soaking time for the melt nor the cooling rate had an appreciable effect on the size or quality of the crystals. Second, the use of very high purity  $\text{TiO}_2$  produced crystals that were lighter in color and had fewer optically apparent domains. Third, platinum from the crucible dissolves in the flux and then precipitates out on cooling. The exact amounts have not been determined.

Current experiments include modifications of crucibles and temperature measuring procedures and variations of the  $\text{Bi}_2\text{O}_3:\text{TiO}_2$  ratios. A cold finger is being welded into the bottom of a large platinum crucible in an attempt to enhance nucleation on the crucible bottom rather than on the melt surface. Constantly monitored thermocouples placed both in the melt and outside the crucible at various positions will be used to gain a better understanding of the effects of temperature and temperature gradients on the growth process.

## 2.2 PLATINATE AND STANNATE FERROELASTICS

(A.S. Bhalla and L.E. Cross)

Isopropyl ammonium chloroplatinate  $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PtCl}_6$  is known to undergo a "martensitic" transition at  $37^\circ\text{C}$ , from an orthorhombic higher temperature structure (space group  $\text{Bbcm}$ ) to a mimetically twinned monoclinic lower temperature phase. The lower temperature twin states may be described as the alternation of a very weak spontaneous elastic shear about the orthorhombic  $[010]$  direction of the higher temperature prototype, and the point symmetries of high and low temperature phases satisfy all requirements for the Aizu ferroelastic species  $\text{mmmF2/m}$ . It is therefore natural to inquire whether the low temperature phase is a true ferroelastic in the sense that the volume or orientation of the shear domains may be altered by a suitably chosen homogeneous elastic driving stress.

Single crystals of isopropyl ammonium chloroplatinate (IPACP) and an isostructural chlorostannate (IPACS) were grown from solution by an unseeded isothermal evaporation technique. The IPACP crystallizes with a platy habit, the major surfaces being perpendicular to the orthorhombic [010] direction, and when viewed in white light, show a deep orange color. IPACS develops more chunky bipyramid shaped crystal, but again the major surfaces are normal to the [010] orthorhombic direction, and these crystals are transparent and colorless in white light.

The orthorhombic (100) appears to be the commonly occurring composition plane (type A twin), but less frequently (001) also appears as composition plane (type C twins). Viewing in polarized monochromatic NaD light along the orthorhombic b-axis [010], the extinction directions are tilted away from the (100) plane by  $\sim \pm 20^\circ$  in the platinate and by  $\sim \pm 6^\circ$  in the stannate. On heating, the twinning disappears abruptly at  $37^\circ\text{C}$  in the platinate and at  $40^\circ\text{C}$  in the stannate, when measured at ambient pressure (1 bar). Under hydrostatic pressure, however, the transition temperatures increase almost linearly with pressure  $\sim 7^\circ\text{C/kbar}$  in IPACP and  $\sim 9^\circ\text{C/kbar}$  in the IPACS crystal.

To verify a ferroelastic response of both A and C type twins, the technique suggested by Maldonado and Meitzler was used. Thin single crystal lamella were cemented to the upper surface of a thick lucite plate, which was then subjected to four point bending. In this manner, approximately uniaxial tension and orthogonal compression was applied to the plate. When the major axis of the stress system was tilted with respect to the [100] direction the twin walls were observed to move, and new double twins could be introduced in heretofore untwinned regions. Both type A and C twins could be moved by stress, and on removing the bending forces a new remanent twin state was observed to persist. The stress level required to move twins or induce new twinning was observed to decrease on raising the temperature towards the transition temperatures.

Frequently it has been observed that both full and partial ferroelastic response is associated with ferroelectric behavior. In IPACP and IPACS, however, dielectric measurements for fields applied along [010] show quite normal low permittivity with a K value of 10.6 in IPACS, a similar low K in IPACP, and no measurable anomaly at  $T_M$ . More significantly, also, a test for optical second harmonic generation using the powder method of Kurtz and Perry showed no harmonic output (SHG intensity less than 1/100th of that obtained from a quartz powder of similar particle size) in either high or low temperature phases of the IPACP, as would be expected for the centric species  $mmmF2/m$ .

It is to be expected that ferroelastic phase transitions should be markedly influenced by elastic stress; heretofore, however, measurements of hydrostatic pressure dependence have been confined to materials such as gadolinium molybdate, Rochelle salt, KDP, etc., which show simultaneous fully ferroelectric and fully ferroelastic behavior. In IPACP and IPACS, however, ferroelasticity is not accompanied by any significant dielectric anomaly, and the species is centric so that both ferroelectric and antiferroelectric behavior are excluded. It thus seemed highly desirable to measure the hydrostatic stress dependence of  $T_M$  in these simple ferroelastic crystals.

Experience showed that it was possible to discern the transition on heating with a reproducibility better than  $\pm 0.5^\circ\text{C}$  dictated largely by the homogeneity of the temperature bath. On cooling, very close mimetic twinning occurring just below  $T_M$  made it more difficult to discern the exact transition point. Since a hydrostatic pressure vessel with optical windows was available it was decided to monitor the phase change under pressure directly in polarized light. To obviate the difficulty of stress induced birefringence in the vessel windows the crystal, polarizer and analyzer were all contained within the pressure medium, the polaroid sheet being fixed in the crossed position at the orthorhombic (prototypic) extinction positions.

The mean values of the temperature dependence in the linear region were

$$(dT_t/dP) = 7^\circ\text{C/kbar in IPACP}$$

$$(dT_t/dP) = 9^\circ\text{C/kbar in IPACS}$$

From the very abrupt loss of twinning and the discontinuous change in monoclinic extinction angle, it appears that the transition at  $T_M$  is first order. Thus it would be expected from the Clausius-Clapyron equation that

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}$$

where  $\Delta V$  and  $\Delta S$  are the volume and entropy changes at  $T_M$ , respectively.

Initial studies of the heat of transition using differential thermal analysis indicate that the transition of  $T_t$  is endothermic, and thus that the entropy change  $\Delta S$  is positive. From the Clausius-Clapyron equation, it is then to be expected that the volume change at the transition should also be positive. Unfortunately, present x ray and thermal data are not sufficiently precise to allow an effective quantitative intercomparison with the experimentally determined pressure derivative of the transition temperature.

### Part 3. MATERIALS FOR CONTROL OF NON-METALLIC SURFACES

#### 3.1 COATINGS BY SPUTTERING

(R. Messier and R. Roy)

A great variety of coatings and films (primarily non-crystalline) can be produced by RF sputtering. This study forms the Ph.D. dissertation of R. Messier. A brief summary follows:

A wide range of non-crystalline solid materials were prepared using the vapor  $\rightarrow$  solid method of RF sputtering including unary and binary oxides, carbides, borides, chalcogenides, and elements. An intensive study of the Ge-Te system led to a better understanding of the structure and properties of materials used in the semiconductor and switching device industries.

The usefulness of the RF sputtering process as an approach to understanding NCS formation was demonstrated. The primary factor controlling NCS formation of sputtered films, and probably all other vapor  $\rightarrow$  solid methods, was the substrate temperature. The only exception found was non-crystalline  $\text{Fe}_2\text{O}_3$  which was apparently controlled by the vapor species. Other factors such as electron, ion, and atomic bombardment of the substrate (inherent in sputtering) and deposition rate were considered. A model was used in which every material has a critical temperature ( $T_c$ ) below which it must obtain in less than a critical time ( $t_c$ ) in order to prevent any crystallization. On the basis of an estimated cooling curve for vapor  $\rightarrow$  solid transitions, this model elucidated the importance of substrate temperature and adequately explained the NCS formation behavior of sputtered, splat-cooled, and water-quenched Ge-Te materials. A measurable parameter was suggested as a relative measure of  $t_c$  for a sputtered material and thus its relative NCS formation tendency. The experimental results were discussed in relation to the various NCS formation theories.

In addition to understanding NCS formation, this study has also been instructive on aspects of RF sputtering in general. For instance, in all cases where the most stable oxide valence state is also the highest (Ti, V, Fe, Nb, Mo, W, Ta), it was easily obtained and was

stoichiometric over a wide range of  $pO_2$ . However, when the most stable valency state was not the highest (Mn, Pb, Ni), stoichiometric films could be obtained only with difficulty. Also it was shown that film properties and structure vary with radial distance, especially directly below the outer edge of the sputtering target. This is important to anyone making devices where reproducibility and uniformity are important. Finally, the large number of parameters and their influence on film structure and properties was clearly demonstrated for Ge. Thus it is not always redundant to investigate systems previously reported since an investigator does not generally explore a wide range of, much less all, conditions.

Several materials have been uniformly deposited on 3mm acid etched Pyrex glass rods by rotating the rods in the sputtering chamber. Coatings of  $MoS_2$  (a lubricant) and SiC (a hard material) were obtained. Both coatings were not sufficiently adherent and did not protect the rods from severe loss of strength in a SiC grit tumble abrasion test. We are currently studying the adherence as a function of post-etch treatment (drying, bake-out, etc.) of the rods.

### 3.2 COATING AND STRENGTHENING OF GLASS

#### 3.2.1 Coatings by Microwave Plasma Assisted CVD

(G.J. McCarthy and J. Mariner)

A number of useful coatings can be produced by chemical vapor deposition but the substrate temperatures are usually too high for application to glass and alkali halides. Using component gases excited by a plasma may allow the CVD reaction to take place at a lower temperature. To produce a plasma of one of the reactant gases we have been using an Evanson 2450 mc cavity with half wavelength guard tubes. This is a foreshortened quarter-wave coaxial cavity with adjustable E mode coupling and stub tuning. Since a 13 mm discharge tube is the largest this cavity can accommodate, we have been placing our substrates in the afterglow region of the discharge. As reported previously, a polymer coating can be produced on glass rods in the afterglow region when

various hydrocarbons are excited to a plasma, the total pressure in the system is  $10^{-1}$  to 5 torr. These coatings adhere better as the temperature of the glass rods during deposition is raised. However, the coatings did not adhere well enough to protect the glass from abrasion damage prior to testing of their bending strength.

In our most recent experiments we have been studying coatings preparation by reaction of two vapor species, one of which has been excited to a plasma by passing through a microwave cavity several inches upstream from the substrate. Again, in order to get a discharge with the apparatus being employed, the total pressure must be maintained at a few torr or less. The second reactant vapor species is introduced just above the substrate which is heated to any desired temperature by an internal wire wound furnace-support combination. Three types of reactions are being considered (the \* indicates the component excited in the cavity):

1. Metal halide + hydrogen\*  $\rightarrow$  metal film
2. Metal halide + oxygen\*  $\rightarrow$  oxide film
3. Silane  $H_2^*$   $\rightarrow$  silicon film

In the basic experiment the gases are reacted on the substrate without plasma excitation and the lowest temperature for appreciable deposition is determined. We then add plasma excitation of one of the component gases and see if equivalent deposition can be obtained at lower temperatures. Thus we hope to establish the plasma contribution to the total energy needed for reaction.

Preliminary results have been obtained using polished silica glass substrates with reaction (1). The reaction of  $TiCl_4 + H_2$  on the substrates heated to  $780^\circ C$  yielded, surprisingly,  $TiO_2$  films (oriented, anatase form by x-ray diffraction). Either the original films were a reactive Ti metal which oxidized on exposure to air or the formation of  $TiO_2$  from traces of oxygen effectively competes with the reduction of  $TiCl_4$  by  $H_2$ . The films had uneven thickness as evidenced by prominent interference rings which could be correlated with the position of the  $TiCl_4$  inlet.



Other experiments using  $\text{SnCl}_4$ ,  $\text{SiCl}_4$ , and  $\text{SiH}_4$  are continuing. In order to derive a plasma discharge in a gas stream at higher total pressures (close to one atm) we are setting up an apparatus using RF coil coupling. The discharge will be located at the heated substrate instead of upstream from it. In some of these experiments we will use organo-metallics as single reactant species.

### 3.2.2 Chemical Strengthening of Glass

(G.J. McCarthy and Marilyn Price)

This method, sometimes called "ion stuffing" or "chemical tempering" is another method of preserving much of the initial strength of glass, in this case by preventing surface flows from spreading to the interior. It could also have application to hardening alkali halides. In a typical experiment with glass, a lithium silicate composition is immersed in a  $\text{NaNO}_3$  molten salt bath for several minutes. Sodium ions replace much of the smaller lithium ions to a distance of several hundred micrometers, leaving the surface in compression. This process has been known for over a decade and considerable research, much of it empirical, has been performed to try to perfect the process. Several products, notably eyeglass lenses, now use chemically toughened glass. A number of problems have prevented more widespread application of this strengthening process. We are examining several of the chemical parameters in our present program. The following parameters are being considered in order to learn more about the process:

1. Effect of glass composition (major and minor components) on depth and concentration of exchange
2. Effect of molten salt composition and additives
3. Nature of the structure of near surface areas before and after exchange

### 3.2.3 Ion Exchange Profiles by Electron Microprobe Analysis

(G.J. McCarthy, Marilyn Price and W.B. White)

It is necessary to have a relatively rapid and reliable method for determining the depth and concentration of ion exchange in order to evaluate each of the parameters just described. The most commonly used

method is to etch away a portion of the surface (depth is determined by weight loss) and chemically analyze for the element under consideration. A direct and nondestructive reading of composition can also be derived from the electron microprobe if appropriate care is taken in sample preparation and data interpretation. In this section of our current study we are evaluating the "probe" for this application. Most of the problems we had initially have been subsequently attributed to operator inexperience or inhomogeneous glass. In fact the probe has turned out to be a very useful tool for determining micrometer size compositional inhomogeneity. By monitoring the signal from two or three elements it is possible to follow the increase in one element and a corresponding decrease in others.

We have been exploring the possibility of using cross-sections of freshly fractured rods instead of mounted, cut, and polished rods to scan for concentration profiles. Our initial experience has been that the time saved in sample preparation is lost in finding and focusing the beam on a section of the glass rod perpendicular to its longitudinal axis.

#### 3.2.4 Ion Exchange in Alkali and Alkali-aluminosilicate Glass

(G.J. McCarthy and Marilyn Price)

Using the probe to determine depth and concentration of ion exchange we have made a number of observations pertaining to the composition of the glass and of the salt bath.

1. The effect of aluminum on  $\text{Na}^+$  exchange in lithium silicate glass is to decrease the depth of penetration of  $\text{Na}^+$  near the surface. Typical depth values for a glass rod exchanged in molten  $\text{NaNO}_3$  are  $220\mu\text{m}$  for lithium silicate and  $165\mu\text{m}$  for the aluminosilicate (7.7 mole%  $\text{Al}_2\text{O}_3$ ).
2. The depth of  $\text{K}^+$  exchange in these same glasses was much less as would be expected from the increased size of the alkali. The effect of  $\text{Al}_2\text{O}_3$  was the same as in (1).  $\text{Rb}^+$  can be exchanged for  $\text{Li}^+$  to a depth of  $4\text{--}6\mu\text{m}$ . Again the effect of  $\text{Al}_2\text{O}_3$  additions to the glass is to decrease penetration but increase near surface concentrations.

3. When a lithium silicate glass is double exchanged, i.e. exchanged first in a  $\text{NaNO}_3$  bath followed by exchange in  $\text{KNO}_3$ , the probe profiles describe the situation clearly. The  $\text{Na}^+$  concentration profile is as expected beyond about  $40\mu\text{m}$ , but is reduced by the  $\text{K}^+$  for  $\text{Na}^+$  replacement toward the surface. The extra heating step causes originally exchanged  $\text{Na}^+$  to penetrate to a greater depth (ca  $350\mu\text{m}$  for  $400^\circ\text{C}$ , 2 hr exchanges in  $\text{NaNO}_3$  and  $\text{KNO}_3$ ).
4. Similar results were obtained for  $\text{K}^+$  exchange in sodium disilicate glass. After 4 hrs at  $400^\circ\text{C}$  in  $\text{KNO}_3$  the  $\text{K}^+$  had penetrated to about  $150\mu\text{m}$ . The effect of  $\text{Al}_2\text{O}_3$  in decreasing penetration while increasing concentration was also observed.  $\text{Rb}^+$  penetrated to about  $12\mu\text{m}$  after two hours in  $\text{RbNO}_3$  at  $400^\circ\text{C}$ .
5. In many of the probe scans the maximum concentration of exchanging ion did not occur right at the edge but at several  $\mu\text{m}$  into the interior. We are checking further on this observation.
6. Small additions of other components to the molten salt bath can affect the depth, concentration and rate of exchange. We have confirmed by weight change measurements that several percent of  $\text{Na}_2\text{CO}_3$  added to  $\text{NaNO}_3$  speed up the exchange. We are now obtaining probe scans to see whether the concentration or the depth of penetration on both are affected.

### 3.3 CRYSTALLIZATION KINETICS OF NON-CRYSTALLINE SOLIDS AND COATINGS

(T. Takamori and R. Roy)

This report is a summary of the Ph.D. dissertation of T. Takamori in which the rapid crystallization behavior of non-crystalline solids with a wide variety of composition was studied experimentally in detail for the first time.

Those non-crystalline solids which are on the borderline of "stability" and can be obtained only by rapid quenching, crystallize quite rapidly at certain temperatures when they are heated at a constant rate. It was first necessary to clarify the significance of this "crystallization temperature" or "Tx" by qualitative arguments and then define it conceptually as the limiting temperature of the "metastably" retainable state under defined conditions, thus drawing a practical borderline between metastable and unstable state. Such a Tx was shown to be determinable experimentally, preferably by a dynamic method such as DTA. A very reproducible result can be obtained if the sample is finely pulverized and a consistent heating rate used.

Experimentally, Tx was defined (tentative) as the extrapolated onset of the exothermic peak of crystallization on the DTA thermogram when the heating rate was 20°C/min. The Tx's of several oxide systems, unary and binary, some chalcogenide glasses and elemental germanium were examined. It was demonstrated that even those glasses which can be obtained only by rapid quenching techniques are retainable up to fairly high temperatures once they are formed into glasses. There is no direct relation between the Tx loci on T-X diagrams and the shape of the liquidus of these systems. One of the most interesting points obtained from the determination of Tx's in such systems was the extrapolation of the Tx curves of binary system to the end members. Significance of such an extrapolation was confirmed on  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  using several binary systems containing either one of them as an end member. The results suggested that, if the  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  "glass" were ever prepared by any quenching technique from liquid, such imaginary glassy  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  would be retainable up to the temperature as high as 900°C or 500°C, respectively. A similar extrapolation was attempted on the Ge-Te glasses and about 10°C was reached for pure Te. These predicted Tx's for  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and Te agree very well with the crystallization data of the vapor deposited films in the literature, lending excellent support to the rather basic nature of Tx as a fundamental materials parameter.

On the basis of the present experiments on the Tx's plus the literature survey, it was inferred that the Tx's are the only parameters necessary for predicting non-crystalline solid retention if the quenching rate is rap'd enough for the formation. On the Ge-Te glasses the Tx locus was shown to be independent of the glass transition temperature Tg on the T-X diagram. From this result plus the literature survey, a general comparison between the Tx and the Tg led us to emphasize that Tx is no less important than the Tg in characterizing non-crystalline solids on the borderline of stability.

The crystallization enthalpy of the materials in the present work were mostly of the order of 1-10 kcal/mole which is comparable to the enthalpy of fusion of many ionic crystals, and somewhat larger than typical rapid phase transitions in solids.

Concerning the mechanism of rapid crystallization, two aspects were considered in the present work: the nucleation on the surface and the cooperative processes in growth. Since most cases of nucleation in solids are heterogeneous, especially at lower temperature, it would be expected that surface-nucleation plays an important role in most crystallizations of non-crystalline solids on the borderline of stability. This has been confirmed, in a way, by the fact that the Tx's determined for the pulverized samples are not sensitive to contamination so that the data have been reproducible through the present work. Some additional evidence for the surface-nucleation has been observed on chalcogenides.

The sharp exotherm at Tx on the DTA thermogram is attributed to the rapidity of crystal growth. In such rapid growth, contribution of cooperative processes cannot be disregarded. The appearance of more than one phase, such as mullite and  $\gamma\text{-Al}_2\text{O}_3$  from the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  glasses and GeTe and Te crystals from the Ge-Te glasses, by one exothermic reaction may also be indirect evidence for such a process being operative.

Some structural studies in connection with or accompanied by the rapid crystallization have been conducted for some systems.

Finally, as a unique kinetics of the rapid crystallization, the "explosive" crystallization of non-crystalline germanium (prepared by RF sputtering) when triggered by a local transient energy pulse was found in the course of this work. The subsequent semiquantitative study on it from various aspects has clarified many features of this phenomenon. One of the best explanations for this phenomenon at the moment seems to be a "cascade-type" energy transfer.

### 3.4 CHARACTERIZATION OF GLASSES AND COATINGS

The characterization of coatings on either crystalline or glassy substrates involves at least the following:

1. Chemical composition
2. Homogeneity
3. Structure

Useful information on the first two may be obtained with the electron probe as previously discussed. The third poses a problem. Crystalline coatings can be characterized by x-ray diffraction techniques. Non-crystalline coatings can be expected to have structural as well as compositional inhomogeneities. There may also be structural and compositional heterogeneities in the outer layers of the substrate such as would occur in ion-exchanged glasses. We have, therefore, made a concerted effort to devise tools for the determination of structure and structural perfection. Of these, Raman spectroscopy has proven a new tool of unusual versatility.

#### 3.4.1 Theory of the High-Frequency Vibrational Spectra of Silicate Glasses

(S. Brawer)

A theory has been developed which relates the high-frequency vibrational spectra (infrared and Raman) of glasses to glass structure. Essentially, the theory enables one to calculate the high frequency ( $>750\text{ cm}^{-1}$ ) vibrational spectra of the random network model of vitreous silica. According to this model,  $\text{SiO}_4$  tetrahedra are connected at the vertices so each silicon is tetrahedrally coordinated by oxygens while each oxygen

is two-fold coordinated by silicon. A continuous three-dimensional random network is formed. The Si-O-Si angle varies more or less randomly between 120 and 160° leading to a lattice with no long-range order.

The central theorem proved is: In a statistically homogeneous random network both the  $1100\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$  peaks in the infrared and Raman spectra are as narrow as in the crystalline silicates. In the pure random network the only detectable broadening is the usual temperature broadening.

Such a narrow line in silica glass has been reported by Simon.

The theory can be extended to alkali and alkali aluminosilicate glasses with less than 10 mole% alumina, less than 10 mole% alkali oxide, and any amount of alkali oxide. This includes many glasses of commercial and scientific importance. The central theorem quoted above is still true for these glasses.

In general, somewhat broader lines than predicted by the theory are observed in the spectra of silicate glasses including silica glass. The theory indicates that the peaks in the vibrational spectra are broadened either by point defects (such as vacancies, interstitials, etc.) and, more importantly, by heterogeneities. A heterogeneous glass is one in which different regions of the glass have different properties, such as density, composition, force constants, structure, etc. Such heterogeneity can be caused by phase separation, different cooling rates in different regions of the glass, and inhomogeneous strains.

The theory leads to the conclusion that it is possible to correlate the widths and frequencies of the high-frequency peaks in the vibrational spectra of glass with the method of preparation, heat treatment and thermal history, as well as composition of the glass.

At present, only experiments correlating vibrational spectra with glass composition have been reported in the literature. These experiments have not taken other variables into account. In view of the many

different glass structures possible in a glass of one given composition due to differing thermal histories, it is small wonder that such experiments have been indeterminate.

Up until now, heterogeneity in glass has been characterized by pictures taken with the electron microscope. The theory developed here suggests that a similar characterization is possible using vibrational spectroscopy, and that a correlation can be made between the spectra and the amount of heterogeneity. Clearly the use of vibrational spectroscopy as a simple, nondestructive and quick method of characterizing glass heterogeneity would be highly desirable.

#### 3.4.2 Raman Spectra of Alumino-Silicate Glasses

(R. DiSalvo, W.B. White, G.E. Rindone, S. Brawer, G.J. McCarthy)

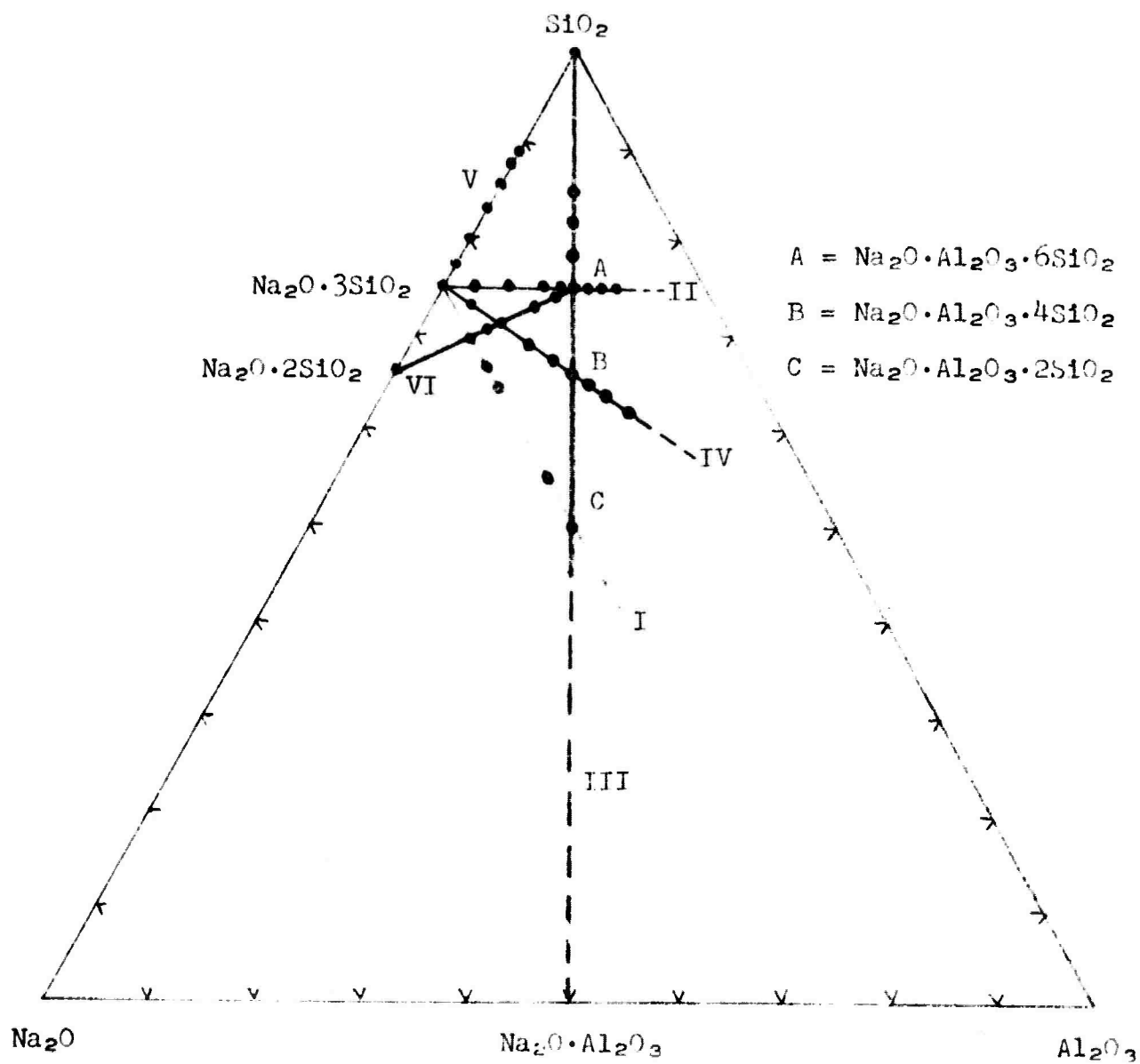
Vibrational spectra have been measured by laser Raman spectroscopy on a variety of soda-alumina-silica glasses (Fig. 1). Compositions have been varied from Al/Na ratio 0.0 to 1.86 and (Na+Al)/Si ratio 0.0 to 2.0 and have been systematically altered so as to reflect changes in Al coordination number and the occurrence of nonbridging oxygens. A typical set of spectra for a particular series of glass compositions is shown in Fig. 2. The spectra show considerable variability with composition, and systematic relations of band position and line width with composition are observed.

The outstanding feature in most of the spectra is the peak present at approximately  $1100\text{ cm}^{-1}$ . This has been assigned to the symmetric Si-O-Si stretching vibration in the glass. As an example of the type of data which can be drawn from these spectra, one can plot the Al/Na ratio vs the observed peak position of this band. Another useful parameter,  $f$ , has been defined by

$$f = \frac{\text{number of nonbridging oxygens}}{\text{number of tetrahedral sites}}$$

This value is also a well behaved function which, when plotted against band frequencies and line widths, is helpful in revealing trends.





Glass Compositions Examined by Laser Raman Spectroscopy  
in the System Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

Figure 1

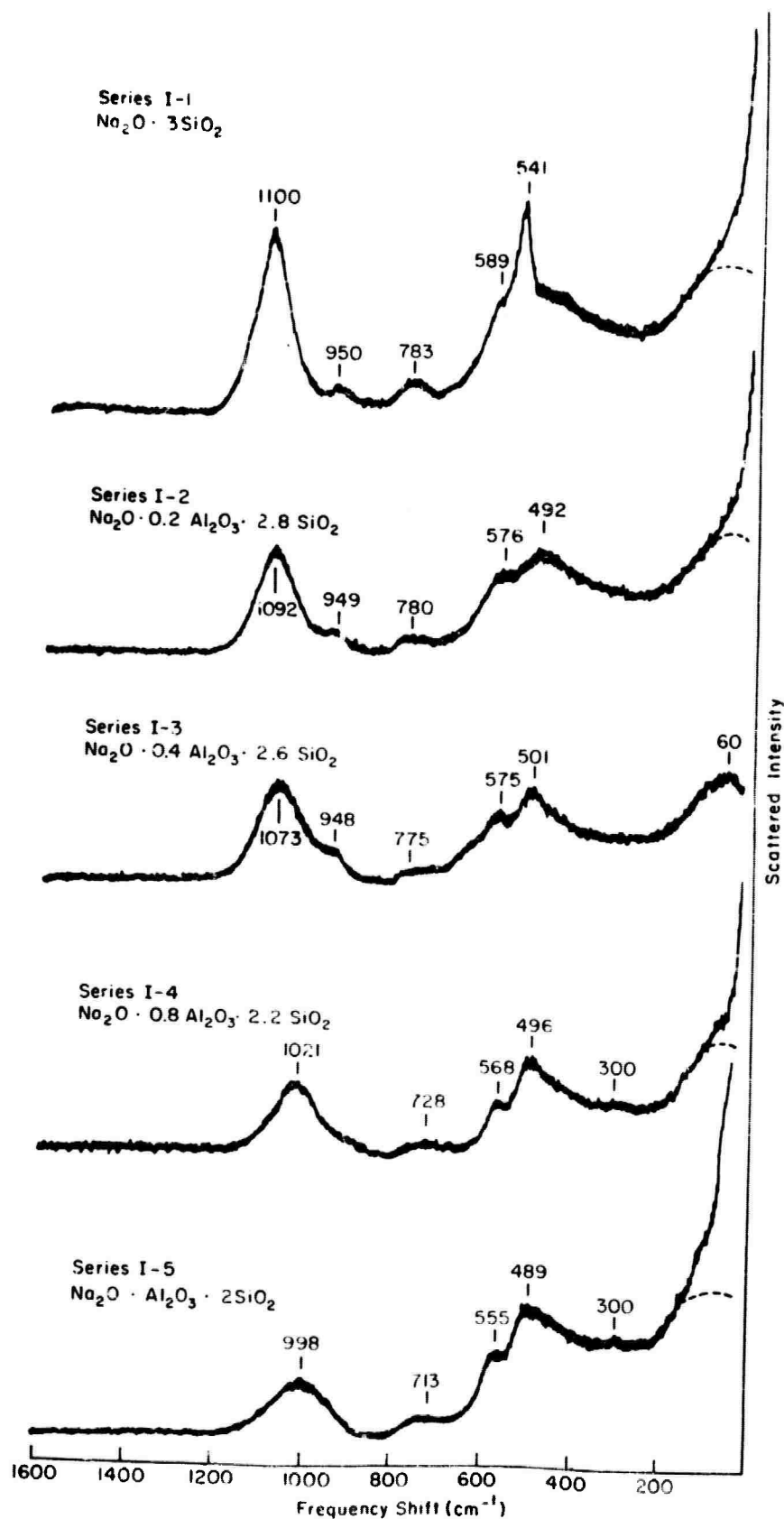


Figure 2. Laser Raman Spectra of Glasses in Series I Having the General Composition  $\text{Na}_2\text{O} \cdot x \text{Al}_2\text{O}_3 \cdot (3-x) \text{SiO}_2$ ;  $x = 0.0-1.0$ . The spectra are vertically displaced for display purposes.

The most important conclusion to date is that one can indeed speak of statistically ordered and statistically disordered states in a glass. When the network consists entirely of silica tetrahedra, sharp, intense Raman lines are observed at high frequencies as predicted. When alumina tetrahedra are randomly substituted, the lines broaden and weaken reflecting the increased degree of disorder and loss of average translational symmetry.

### 3.4.3 Characterization of Real Surfaces by Laser Mass Spectrometry (B.E. Prox and E.C. Beahm)

Results obtained in laser mass spectrometric studies of inorganic solids were analyzed in terms of three processes: vaporization, ionization, and vapor expansion-vapor reaction. In these studies a solid state (ruby or neodymium glass) laser operating in the normal mode with an output of  $10^5$  to  $10^6$  W/cm was coupled with a time of flight mass spectrometer. A simple steady state vaporization model was used. In this model the laser vaporizes the sample surface in a steady manner producing a crater. Ions for analysis in the mass spectrometer can be generated by the laser beam interacting with the sample and by mass spectrometer filament electrons of a specified energy. Experimental results and theoretical analysis show that thermal ionization can be assumed to be the major source of primary ions which result from laser photon absorption by the sample. Thermal ionization in the laser mass spectrometer is best expressed by a "modified" Saha-Langmuir type equation incorporating the observed ratio of two ionic species, the difference in their ionization potential, the ratio of their concentrations in the solid, and a correction factor.

For most results obtained with the mass spectrometer detecting only ions generated by laser interaction, the ionization potential of the vaporized species dominates over vaporization in determining the observed intensities.

The rapid expansion of vapor from the sample surface is similar to isentropic expansion through an orifice, which results in rapid cooling. Because of this cooling, reactions with large positive

energies of activation will be quickly quenched. However, recombination reactions and condensation as well as ion-molecule reactions have negative or zero temperature coefficients and may be accelerated by the decrease in temperature. The result will be clusters of large species such as those commonly seen in laser mass spectrometric studies.